

FINAL REPORT

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European Research Office - US Army
US Office of Naval Research - Europe

**First European Tri-Service Advanced Materials Workshop:
*Compressive Strength in Rigid-Rod Polymers***

The Workshop was held at Pembroke College, University of Cambridge on 3-5 September, 1992 with 23 participants (list attached). The programme (also enclosed) called for a series of lectures from invited speakers for the first day and a half. These were delivered and received with considerable enthusiasm and discussion. In the afternoon of the second day three sets of small groups provided the format for detailed discussion of points raised in the earlier lectures. This proved to be critical and of much value to all attendees. These discussions lasted the entire afternoon. The leader of each discussion group prepared a summary of questions and ideas generated in their group and on the last morning (Saturday) each leader presented this summary to all participants with general discussion following. All sessions (lecture, small group and large group) were integral to the success of the Workshop and all were actively part of the give-and-take which distinguished the Workshop.

Gerhard Wegner began the Workshop with an intriguing and provocative presentation of experimental work on model LC polymer systems which emphasized the importance of chain segregation according to chain length. His morphological studies set the stage for much debate on molecular origins of compressive failure. Steve Allen followed with a presentation of a review of Du Pont research on strategies for possible improvements in compressive strength in rigid-rod polymers. It offered an insight into the scope and depth of the long term efforts of a key company with a commercial product in this field. Ian Ward was next with a detailed presentation of mechanical behaviour of PBI and the role of water on such properties. The next lecture was by Jim Economy who gave a progress report on DARPA/ONR supported research on factors affecting compressive properties of high performance composites including both organic and inorganic polymer systems. In the final presentation of the first session M Northolt gave a particularly plausible defense for the hypothesis that improvement of compressive strength of polymeric fibres will require covalent crosslinks.

The Thursday afternoon session began with Fred Arnold's lecture on the wide variety of chemical approaches taken at the Air Force Wright Laboratory over the past several years and the evaluation of the effect of chemical structure on compressive properties. Professor Ruland's lecture was to have been next, but

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had to be cancelled due to his illness which prohibited his participation at the Workshop. Jay Im followed with a talk on PBO fibres. He emphasized the compressive strength test methodology and the associated fibre failure modes. Bob Young then gave a presentation on the use of Raman spectroscopy in the evaluation of compressive properties of fibres. He proposed that his data is consistent with Euler Buckling as the mechanism for failure in these fibres. The final presentation of the Thursday afternoon session was R Hentschke's lecture on the power and limitations of molecular dynamics computer simulations as an aid in understanding compressive strength in fibres of highly oriented polymers.

The Friday morning session was begun by G Marrucci as he discussed the rheology (shear flow) of rigid-rod polymers and the effect of tumbling on defects and disclinations in these systems. Yachin Cohen then presented a detailed description of the coagulation of rigid-rod polymer solutions with water. He proposed that for these polymers collective buckling of the microfibrils is responsible for compressive failure. H Fischer followed with a report of recent work done at Bristol on the phase diagram of the PBZT/PBO-P₂O₅-H₂O system and its influence on ultimate compressive strength of fibres processed therefrom. Dusan Prevorsek gave a lecture on compressive failure in ultra-strong polymers from the point of view that the microfibrillar structure is crucial to proper control of these properties. The final lecture was that of Alan Windle in which he presented chemical and structural details for a family of carbuncular rigid-rod polymers designed to pack isotropically, thereby offering the possibility of improved compressive strength.

On Saturday morning each of the group leaders from the previous afternoon presented, on overheads, the essential points of debate and resulting conclusions or questions raised during their small group sessions. A copy of the overheads is enclosed. They present an excellent reflection of the discussions which accompanied their presentation on Saturday morning. The scientific exchange was lively and far-ranging. I feel that the Workshop was highly successful. In addition to providing a full general debate on the subject, it is surely likely that research ideas were generated by each participant toward which their own special expertise can be applied. Key questions were raised with the various research strategies for solution to the compressive strength problem being presented in the large group overheads - copies enclosed.

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A C Griffin (Workshop Organiser)
 Melville Laboratory for Polymer Synthesis
 University of Cambridge
 2 December 1992

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FIRST EUROPEAN TRI-SERVICE ADVANCED MATERIALS WORKSHOP

"Compressive Strength in Rigid-Rod Polymers"

Pembroke College
Cambridge

Preliminary Schedule

September 2, 1992, Wednesday

pm Arrival in Cambridge (trains depart for Cambridge half-hourly from London Kings Cross and Liverpool Street stations)

Check-in at Pembroke College (located on Trumpington Street; taxi from station costs about £3.00; no parking available at the College). Please report to the Porters Lodge where room keys will be issued.

7.30pm Dinner in Hall, Pembroke College

September 3, 1992, Thursday

8.15am - 9.00am Breakfast

9.00am - 9.15am Introductory Remarks - Dr A C Griffin

9.15pm - 12.30pm Lectures and Discussion (I); Coffee break

12.30pm - 2.00pm Lunch

2.00pm - 4.30 pm Lectures and Discussion (II); Tea break

7.30pm Dinner

September 4, 1992, Friday

8.15am - 9.00am Breakfast

9.00am - 12.30pm Lectures and Discussion (III); Coffee break

12.30pm - 2.00pm Lunch

2.00pm - 4.30 pm Small Group Discussions; Tea break

7.30pm Banquet

September 5, 1992, Saturday

8.15am - 9.00am Breakfast

9.00am - 12.30pm Large Group Discussions, Recommendations, Wrap-Up; Coffee break

12.30pm - 2.00pm Lunch

All sessions of the Workshop will be held in the Old Library at Pembroke College.

Supported by USAF European Office of Aerospace Research and Development; US Army Research, Development and Standardization Group, UK; Office of Naval Research European Office.

Workshop Lecture Schedule

3 September, Thursday (am)

Session I

| | | | |
|-------|---|-------|----------------------------------|
| 9.15 | - | 9.45 | Professor Dr G Wegner |
| 9.45 | - | 10.15 | Professor I M Ward |
| 10.15 | - | 10.45 | Dr S R Allen |
| 10.45 | - | 11.00 | Coffee Break |
| 11.00 | - | 11.30 | Professor J Economy |
| 11.30 | - | 12.00 | Dr M G Northolt |
| 12.00 | - | 12.30 | Discussion of Session I Lectures |

3 September, Thursday (pm)

Session II

| | | | |
|------|---|------|-----------------------------------|
| 2.00 | - | 2.30 | Dr F E Arnold |
| 2.30 | - | 3.00 | Professor Dr W Ruland |
| 3.00 | - | 3.30 | Dr J Im |
| 3.30 | - | 3.45 | Tea Break |
| 3.45 | - | 4.15 | Professor R J Young |
| 4.15 | - | 4.45 | Dr R Hentschke |
| 4.45 | - | 5.15 | Discussion of Session II Lectures |

4 September, Friday (am)

Session III

| | | | |
|-------|---|-------|------------------------------------|
| 9.00 | - | 9.30 | Professor G Marrucci |
| 9.30 | - | 10.00 | Dr Y Cohen |
| 10.00 | - | 10.30 | Dr H Fischer |
| 10.30 | - | 11.00 | Coffee Break |
| 11.00 | - | 11.30 | Dr D C Prevorsek |
| 11.30 | - | 12.00 | Professor A H Windle |
| 12.00 | - | 12.30 | Discussion of Session III Lectures |

Small Group Discussion

A. Keller

Compressive Modulus

- 1) Its Meaning?
- 2) Its Measurement.
- 1) In terms of Morse potential.
More complex molecular arrangements,
Is it identical to tensile modulus?
Over what strain range?
 - i) Linear portion - elastic
 - ii) Non-linear - "
 - iii) Recoverable but only with timeWhich of i)-iii) is taken & by whom?

Other issue:

Genuine compression vs. buckling (elastic)

How do we know which when measuring?

- 2) Need for exact definition of test method.
(Joe Magill's point)

II Compressive Strength

Initiation of failure?

Statistical onset of local shear

Kink bands (in general)

Twinning (in particular)

What happens on molecular level?

How chains kink? Over what distance?

Analogies & Differences
carbon fibre.

2 dimensional vs. 3 dimensional
In C planar orientation throughout fibril.

On Skin - Core Effect

Orientation different. Where does fracture start?
Within skin or within core?

Micro fibril

Intrinsic or statistical?

Cohen: Intrinsic

Does not change with processing.

Can it relate to crystal solvate? As it goes
through crystal solvate it should.

In general due to inhomogeneous contraction
coagulation with special agency of crystal solvate.

Morphology (in general)

What is our baseline?

Stationery System

Cohen: spherulites, lamellae
(all crystal solvate)

On solvent removal lamellae break-up in bundles.
Can this have connection with fibrils in oriented systems?

On origin of low angle maxima: 4 point pattern

Additional (omitted from p.!))

Role of chain ends? In register (like Wegner)
or randomly distributed? Examples for both!

REPORT OF GROUP DISCUSSION ①

— R. J. YOUNG

1. CONTROL OF COMPRESSION STRENGTH

1.1 Intermolecular forces

Most over-riding factor is chemical structure/bonding

eg Ranking of compression strength

$Al_2O_3 > C > Aramid > Rigid rods > Polyethylene.$

1.2. Microstructure

Manipulation of the microstructure of a given material may change compressive strength by factor of up to 3 \therefore Secondary factor

eg Cross-linking appears to show some promise but it may degrade tensile properties

2. MECHANICS / MECHANISMS OF FAILURE

(2)

Probably Euler Buckling initiated at the fibril level

∴ Might improve behaviour by

- Changing aspect ratio of the fibrils
- Binding the fibrils together laterally

However, even if the easy Euler Buckling mode is a suppressed failure will occur through shear or twinning within the crystallites

cf Polydiacetylene
Single crystals



NB. Shear by chain slip may be suppressed by

- Radiation-induced cross-linking
- Interchain, 2-D Hydrogen bonding

But Both of these will probably degrade the tensile properties

3. INFORMATION MISSING/NEEDED

3.1 Compressive modulus

It is clear that the modulus of the fibres is not unique. It changes continually going from tension to compression due to

- a) The inherent properties of the molecules
- b) The reorganisation of the microstructure

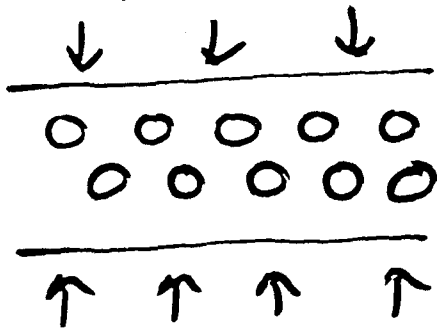
We need accurate and reliable estimates of modulus versus strain

eg Raman spectroscopy - promising estimates

or: Microtension/compression testing on single filaments
- difficult but could be helpful when compared with Raman.

3.2 Lateral Compressive Properties.

We have been concerned only with axial compression of fibres but in some applications lateral compression is important



eg Side impact of a uniaxial composite

4. FUTURE PROJECTS - THE WAY FORWARD ?!

Can we learn anything from other technologies?

4.1 Nature

It might be helpful to examine natural structural materials with good compressive properties

eg Wood (good for aircraft!)

Are hollow fibres more resistant to Euler Buckling?

4.2 Carpet fibres

It is possible to improve compressive properties by changing the geometry of the fibre cross-section.

(increase the moment of inertia)

eg Clover-leaf section



Widely used for carpet fibres
They spring back when compressed axially! Resistant to Buckling

NB: May be possible with Thermotropics but would be difficult with Lyotropics

Discussion Group

Compressional Strength (CS) of G. Wegner

What is it?

- Shear Yielding vs Brittle Fracture
- Ductile Deformation

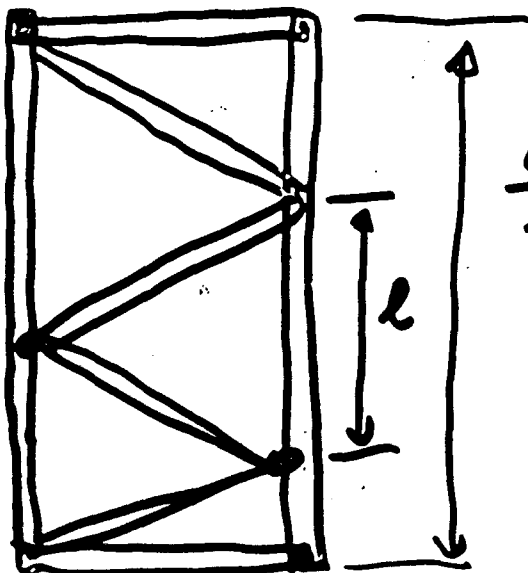
Stress-Strain in Compression \equiv in Tension!!

\Rightarrow SHEAR-MODULUS the important magnitude
→ EULER-BUCKLING

HOW TO INCREASE (CONTROL) SHEAR-MOD.

~~REMEMBER~~

1. Possibility: Cross-Buckling



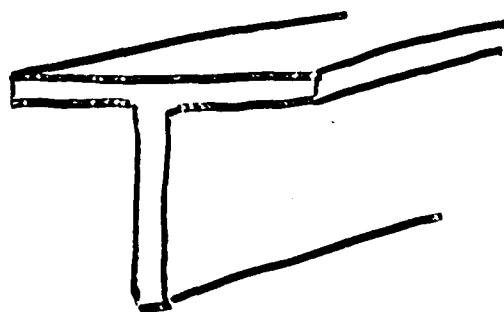
$$\frac{L}{l} = N_c ?$$

$$N_c \geq 10 ??$$

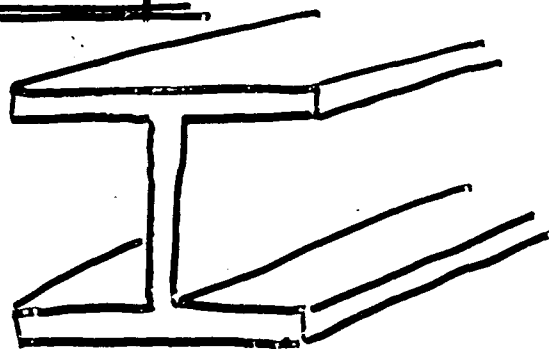
Limitations:

- Chemistry of crosslinking:
 - no volatiles
 - no degradation of stress bearing chains
 - no cross change of structure (X allinity...)
- Introduction of X links limits Number of chains / X section \rightarrow reduction in tensile strength
- 3-D structure ought to be achieved
- Processing

2. Possibility: Molecular shape

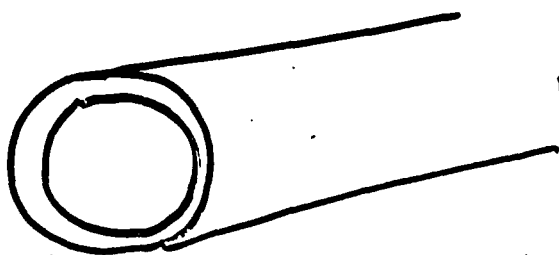


T-Bar



H-Bar

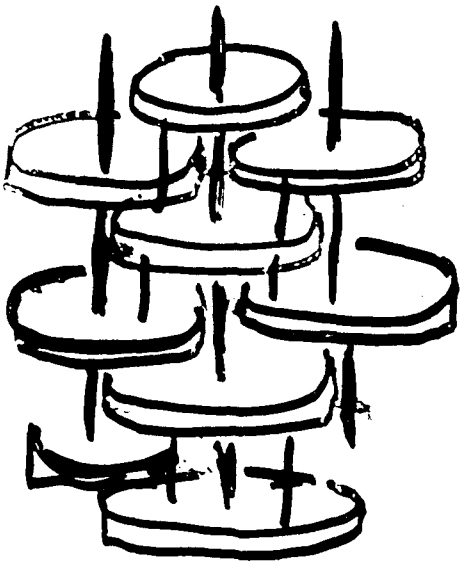
- Increase compressive strength at molecular level
- Problems at the level of fibres \rightarrow shear mod.
- Synthetic problems, processing properties??



Hollow fibre molecules

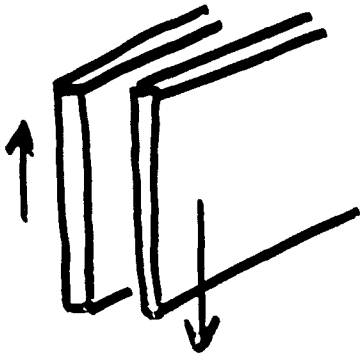
3. Possibility: Prevent Glide planes

— Interlocking of macromolecules

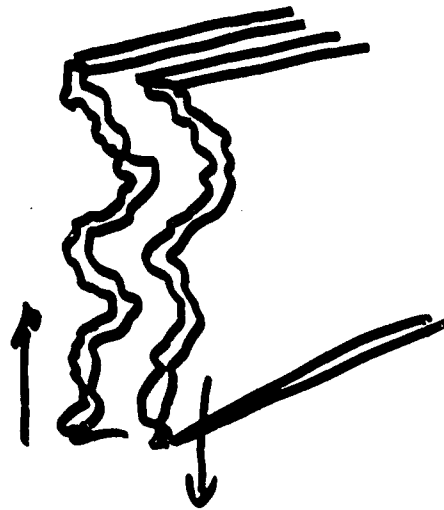


- Dimensionality
- N of chains / X section low

— Generalization:



vs



4. Possibilities: Fillers

— does not make sense

5. Surface treatments:

limited success → tension

→ brittle fracture

Would diamond-fibre be good?

→ Limits of shear modulus

Calculations possible??

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